ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 6, pp. 1141–1145. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © O.E. Zhuravlev, V.M. Nikol'skii, L.I. Voronchikhina, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 6, pp. 960–965.

# Physicochemical Properties of an *N*-Decylpyridinium Tetrachloroferrate Ionic Liquid

**O. E. Zhuravlev, V. M. Nikol'skii, and L. I. Voronchikhina**

*Tver State University, Sadovyi per. 35, Tver, 170002 Russia*
*e-mail: pifchem@mail.ru*

Received October 7, 2013

**Abstract**—A low-temperature ionic liquid *N*-decylpyridinium tetrachloroferrate was synthesized. The temperature dependences of density and viscosity of the synthesized ionic liquid, as well as its thermal stability and magnetic properties were studied. The response of *N*-decylpyridinium tetrachloroferrate to magnetic field was visualized, and its structure was calculated at the DFT/ B3LYB/6-31G(d,p) level of theory.

**Keywords**: ionic liquids, synthesis, paramagnetism, quantum-chemical calculations, thermal stability

**DOI:** 10.1134/S1070363214060152

Ionic liquids exhibit such valuable properties as high electrical conductivity and thermal stability, catalytic activity, low vapor pressure, good solvent ability, nontoxicity, and inflammability. In this connection the number of publications on the structure, physicochemical, and electrochemical properties of ionic liquids tends to grow from year to year [1–5]. Certain representatives of this class of compounds have found industrial application in the production of polymeric and composite materials, high-capacity accumulators, condensers, etc.; ionic liquids are also used as catalysts [6–10].

In 2004 Japanese researchers [11] synthesized 1,3-dialkylimidazolium tetrachlotoferrate ionic liquids which responded to magnetic field, because they contained a paramagnetic anion $FeCl_4^-$. Such compounds were given the name magnetic ionic liquids. The term "magnetic ionic liquids" is slightly arbitrary, because real magnetic liquids have orders-of-magnitude higher magnetic susceptibilites. Therefore, the term "paramagnetic ionic liquids" seems to be more correct.

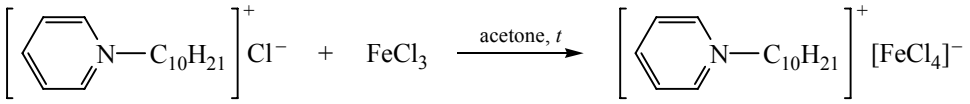
In further works [12, 13] published almost immediately after the mentioned work, the low-temperature ionic liquid 1-butyl-3-imidazolium tetrachloroferrate was proposed to be used as a buffer medium for controlling diamagnetic objects in magnetic field. Evidence for a high catalytic activity of *N*-alkylpyridinium and 1,3-dialkylimidazolium tetrachloroferrates was obtained in [14, 15]. We previously studied the thermal stability and antimicrobial activity of a series of 1,3-dialkylimidazolium, *N*-alkylpyridinium, and tetraalkylammonium tetrachloroferrates [16, 17] *N*-Decylpyridinium tetrachloroferrate is similar in physicochemical properties to 1-butyl-3-methylimidazolium tetrachloroferrate but is less costly and easier to prepare. The physicochemical properties of *N*-alkylpyridinium tetrachloroferrates have been scarcely studied.

In the present work we have studied the physicochemical properties of the paramagnetic ionic liquid *N*-decylpyridinium tetrachloroferrate and optimized its structure by quantum-chemical calculations.

For the starting compound to synthesize this ionic liquid we chose an accessible *N*-decylpyridinium chloride (Scheme 1).

Modern quantum-chemical calculations allow fairly correct prediction of the principal properties of molecules, including their electronic and geometric structures. There have been only a few papers devoted to quantum-chemical calculations of the structure of ionic liquids, and most of them dealt with 1,3-dialkylimidazolium ionic liquids [18, 19]. We performed full geometry optimization of *N*-decylpyridinium tetrachloroferrate at the B3LYP/6-31G(d,p) level of theory using PC-GAMESS/Firefly suit [20]. The optimized structure is shown in Fig. 1.

**Scheme 1.**




As known, hydrogen bonding between atoms is possible if the interatomic distance is shorter that the sum of the van der Waals of these atoms. As seen from the calculated geometry, the interactomic distances $H^{7}\cdots Cl^{1}$ (2.798 Å), $H^{4}\cdots Cl^{1}$ (2.594 Å), and $H^{5}\cdots Cl^{3}$ (2.794 Å) are shorter than the sum of the van der Waals radii of Cl and H (≈3.0 Å). The $Fe^{1}$–$Cl^{1}$ and $Fe^{1}$–$Cl^{3}$ bonds are elongated compared to $Fe^{1}$–$Cl^{2}$, which is explained by interaction of $Cl^{1}$ and $Cl^{3}$ with pyridinium ring hydrogens. Most likely, the hydrogen bonding with the tetrachloroferrate anion involves the α- and β-hydrogen atoms of the pyridinium ring. The cation–anion interaction energy is 412.92 kJ/mol. The energy of intermolecular interaction for this system is much higher than the energy of a hydrogen bond (10–100 kJ/mol) and compares with the energy of a covalent bond, which is explained by fairly strong Coulomb interactions and formation of several intermolecular hydrogen bonds.

Analysis of the IR spectrum of *N*-decylpyridinium tetrachloroferrate in the range 400–4000 $cm^{-1}$ allowed assignment of its characteristic absorption bands.

The visible absorption spectra of *N*-decylpyridiium tetrachloroferrate solutions contain three maxima at 534, 619, and 688 nm (Fig. 2), assignable to the tetrachloroferrate anion [11].

The highest intensity is observed at λ 534 nm. The optical density at 534 nm linearly varies with the concentration of *N*-decylpyridinium tetrachloroferrate (correlation coefficient 0.9939), implying fulfillment of the Bouguer–Lambert–Beer law. The molar absorption coefficient ε was estimated at 1609 ± 320 L $mol^{-1}$ $cm^{-1}$.

The temperature dependence of the density and viscosity of *N*-decylpyridinium tetrachloroferrate in the temperature range (298–338 K) ± 0.5 K showed that these parameters decrease with increasing temperature, which is quite important in terms of practical application. The plots of density and absolute viscosity against temperature are shown in Fig. 3). The temperature dependence of density is linear (correlation coefficient 0.9984), whereas the viscosity of the ionic liquid decreases exponentially with temperature (correlation coefficient 0.9991).

An indirect estimate for the structural stability of a liquid or a solution is provided by the activation energy of viscous flow, i.e. the energy required for a molecule to pass into a new equilibrium state. From the temperature dependence of viscosity we calculated the activation energy by the Arrhenium formula (1) in the temperature ranges $T_1$ and $T_2$ (298 and 338 K).

$$E_a = R\frac{T_2T_1}{T_2 - T_1}\cdot \ln\frac{\eta_2}{\eta_1}. \qquad (1)$$

Here $R$ is the universal gas constant and $\eta_2$ and $\eta_1$, viscosities of the liquid at $T_2$ and $T_1$, respectively.

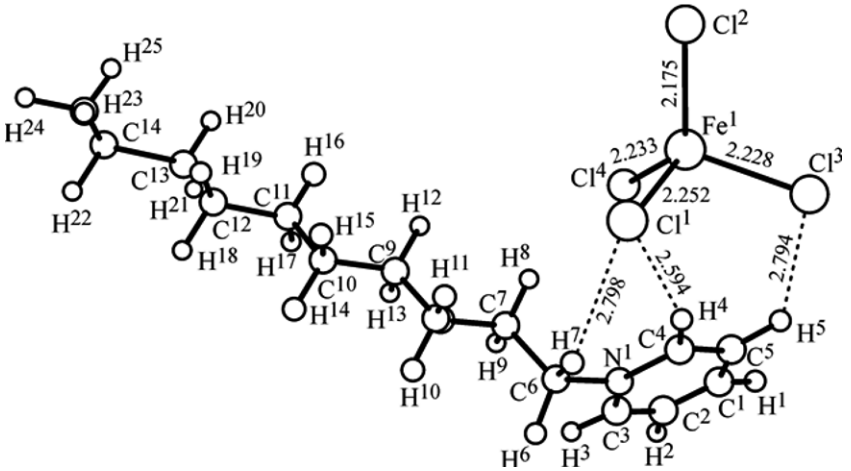



**Fig. 1.** Optimized structure of *N*-decylpyridinium tetrachloroferrate.

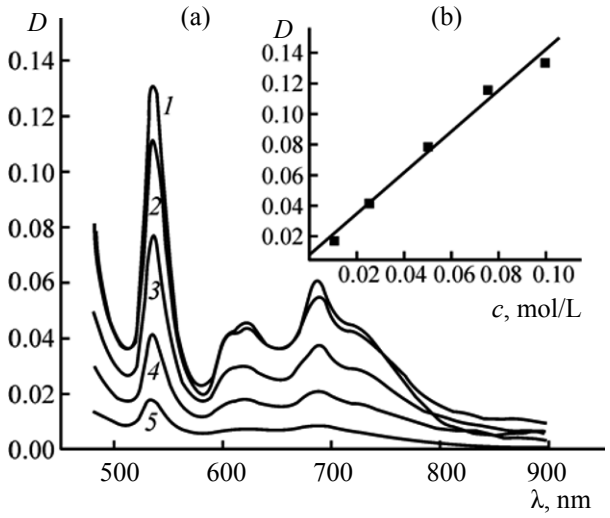



**Fig. 2.** (a) Visible absorption spectra of *N*-decylpyridinium tetrachloroferrate in acetone and (b) dependence of optical density on concentration, M: (*1*) 0.1, (*2*) 0.075, (*3*) 0.05, (*4*) 0.025, and (*5*) 0.01.

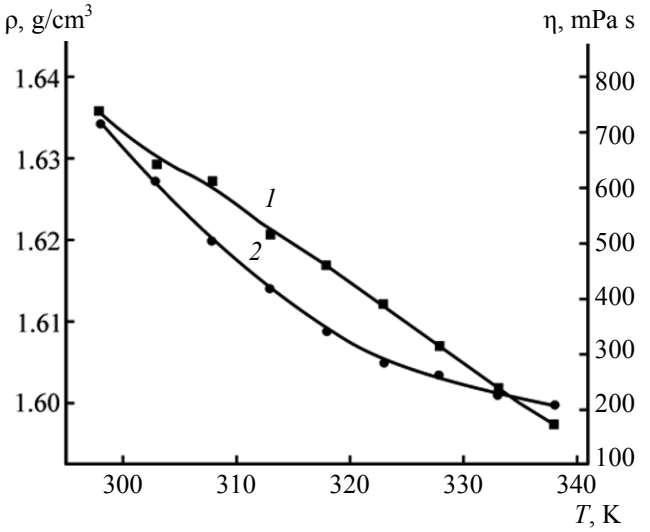



**Fig. 3.** Dependences of (*1*) dansity and (*2*) absolute viscosity on temperature for *N*-decylpyridinium tetrachloroferrate.

The activation energy of viscous flow for the ionic liquid in study is 26.3 kJ. The calculated activation energy of viscous flow for *N*-decylpyridinium tetrachloroferrate is close to the activation energies for polymer solutions [21]. This fact is likely to be explained by fairly strong Coulomb cation–anion interactions, as well as noncovalent interactions like hydrogen bonding. Evidence for this suggestions comes from the quantum-chemical calculations performed in the present work (Fig. 1).

One of the most important properties of *N*-decylpyridinium tetrachloroferrate is its ability to respond to magnetic field, because it contains a paramagnetic anion $FeCl_4^-$. The specific magnetic susceptibility of this ionic liquid is $35.8 \times 10^{-6}$ cm$^3$/g, which is close to the respective values for concentrated solutions of Fe(III) salts. Measurements of the magnetization of *N*-decylpyridinium tetrachloroferrate under external magnetic field (Fig. 4a) revealed no signs of hysteresis. This finding provides evidence showing that the synthesized paramagnetic ionic liquid is a pure paramagnetic and contains no ferromagnetic admixtures. The dependence of magnetic moment on temperature is linear and adheres to the Curie–Weiss law (Fig. 4b).

Visual examination of the system oil–paramagnetic ionic liquid shows that even a weak permanent magnet (magnetic field strength 0.2 T) would suffice to observe attraction of the parmagnetic ionic liquid in the cell (*l* 1 cm). Figure 5 presents the images illustrating the response of our synthesized *N*-decylpyridinium tetrachloroferrate to magnetic field. Oil was added to the system for better visualization.

In view of the fact that in certain organic reactions ionic liquids are used at elevated temperatures, we considered it important to study their thermal stability. Depending on the nature of the cation and anion, ionic liquids exhibit different thermal stabilities. We performed thermal gravimetric analysis of *N*-decylpyridinium tetrachloroferrate (Fig. 6). The compound is stable up to 360°C and decomposes in two stages in the range 360–540°C. The first stage at 360–430°C involves is accompanied by a 60% weight loss. At the second stage at 430–540°C, further 20% weight loss occurs. The rest 20% remain undecomposed at 550°C, we did not analyzed this residue in the present work.

## EXPERIMENTAL

The IR spectra were recorded on a Bruker Equinox 55 FTIR spectrometer for thin films between $CaF_2$. glasses. Elemental analysis was performed on a Hewlett–Packard 185 C,H,N analyzer. The visible absorption spectra were obtained on a LOMO SF-56 spectrophotometer in acetone in the concentration range 0.1–0.01 M, using 1-cm cells. Differential thermal analysis was performed on a Netzsch STA 449 F3 instrument under a stream of air, temperature range 25–550°C, heating rate 5 deg/min. The dependences of magnetic susceptibility on temperature and of mag-

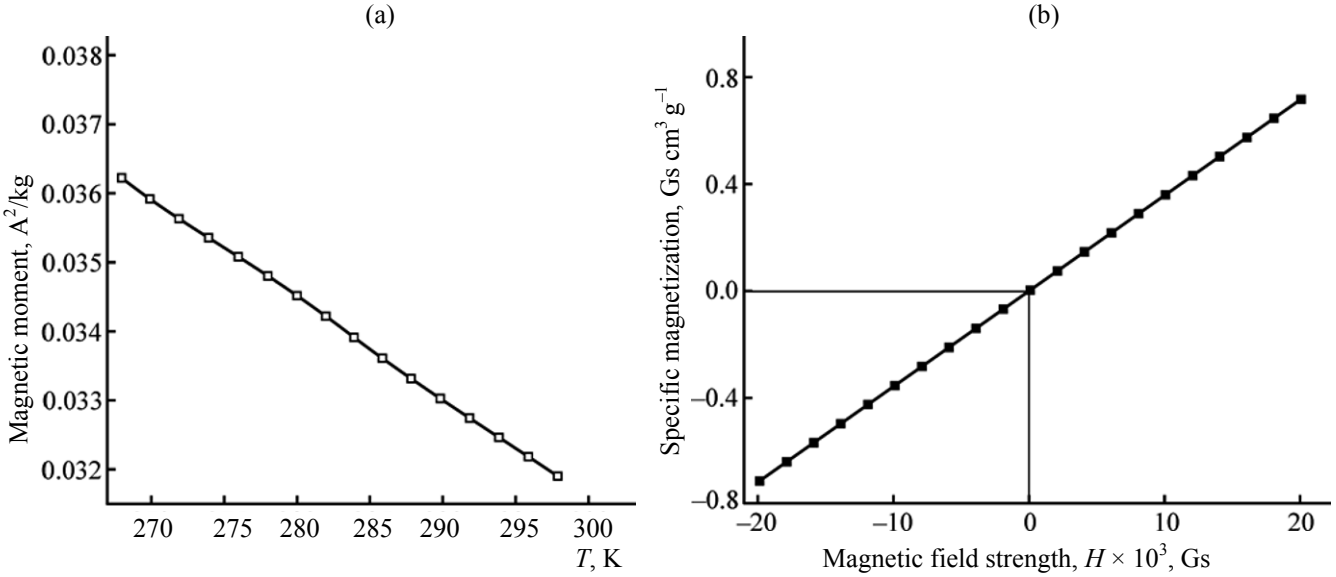



**Fig. 4.** Dependences of (a) specific magnetization on magnetic field strength and (b) magnetic moment on temeprature for *N*-decylpyridinium tetrachloroferrate.

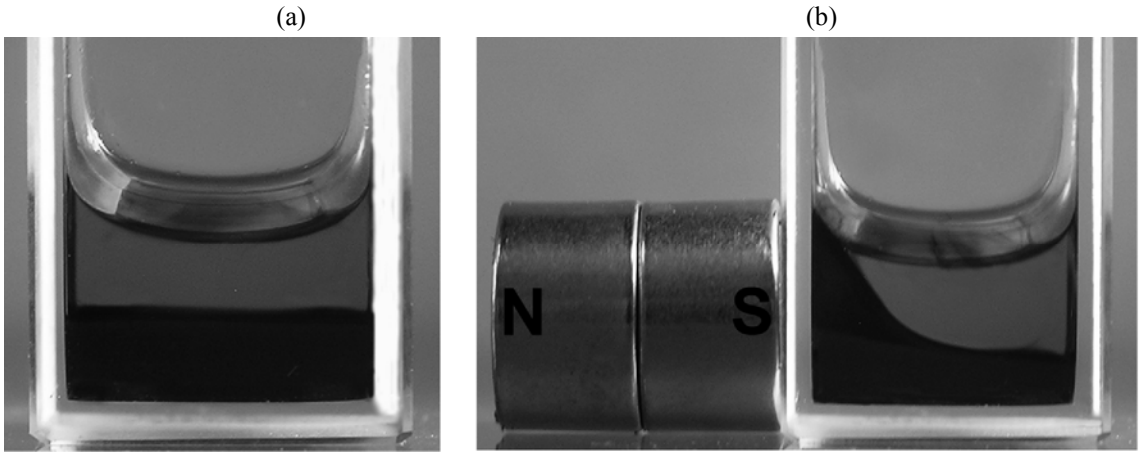



**Fig. 5.** Behavior of the ionic liquid (bottom layer)–oil (top layer) system (a) before and (b) under exposure to permanent magnet.

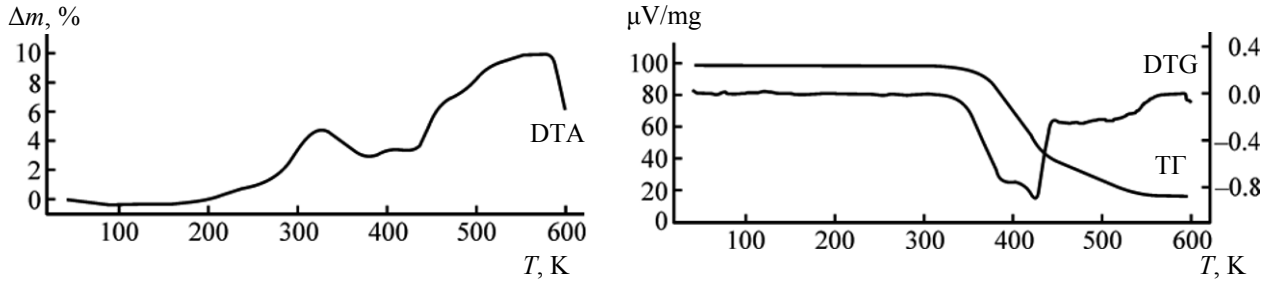



**Fig. 6.** Thermal analysis of *N*-decylpyridinium tetrachloroferrate in air.

netic susceptibility on applied magnetic field were obtained on a SQUID Oxfords Instruments magnetometer in a superconducting solenoid with the maximum field strength of 8 T. Viscosity measurements were performed using an Ostwald viscometer (capillary diameter 1.8 mm). The viscometer was chosen so that the flow time was 70–110 s to ensure a Poiseuille flow. The densities were measure with a picnometer at 25°C by a standard procedure. The absolute viscosity was calculated by Eq. (2).

$$\eta = \tau d K. \quad (2)$$

Here $\tau$ is the flow time, s; $d$ , density, g/cm$^3$; and $K$, voscometer constant.

Commercial *N*-decylpyridinium chloride of chemical grade was twice recrystallized before use from acetone–ethyl acetate (2 : 1), washed with a cold absolute ether, and dried in a vacuum over calcium chloride. mp 64–66°C.

***N*-Decylpyridinium tetrachloroferrate.** Hot acetone solutions of $FeCl_3$ (0.05 mol) and *N*-decylpyridinium chloride (0.05 mol) were mixed, and the mixture was heated under reflux with constant stirring for 10–15 min. The acetone was evaporated, and the residue was dried in a vacuum over $P_4O_{10}$ for 1 day to obtain 95% of the target product as a dark green liquid soluble in water (strongly hydrolyzes, because the $FeCl_4^-$ anion is unstable in aqueous soluitons) and other polar solvents (ethanol, acetone, acetonitrile), *M* 418.03, $\eta$ (25°C) 719.5 mPa s, $\eta$ (65°C) 205.3 mPa s, $d^{25}$ 1.636 g/cm$^3$, $d^{65}$ 1.597 g/cm$^3$, mp 10°C, decomp. point. 360°C. Found, %: C 43.3; H 6.5; N 3.5. $C_{15}H_{26}Cl_4FeN$. Calculated, %: C 43.1; H 6.3; N 3.4.

IR specrum (KBr), $\nu$, cm$^{-1}$: 3055 (C–$H_{arom}$), 2978, 2843 (C–$H_{alif}$), 1648, 1515, 1458 (C–$C_{arom}$), 765, 680 [$\delta$(C–$H_{alif}$)].

## ACKNOWLEDGMENTS

The authors are grateful to staff members of the Devision of Physicichemical Analysis, Center for Collective Use, Tver State University, for performing thermal analysis.

The work was financially supported by the "Scientific and Scientific-Pedagogical Personnel of the Innovative Russia" for 2009–2013 (agreement no. 14.B37.21.0653).

## REFERENCES

1. Welton, T. and Wasserscheid, P., *Ionic Liqids in Synthesis*, Weinhem: Willey-VCH, 2009.
2. Rogers, R. and Seddon, K., *Ionic Liquids: Industrial Applications to Green Chemistry*, Washington: Kluwer Academic, 2002.
3. Dupont, J. and Suares, P., *Chem. Rev*., 2002, vol. 102, p. 3667.
4. Ignat'ev, N.V., Vel'ts-Birman, U., and Vil'ner, H., *Ross. Khim. Zh*., 2004, vol. 68, no. 6, p. 36.
5. Rogers, R. and Seddon, K., *Science*, 2003, vol. 302, p. 792.
6. Yong, W. and Hong, Y., *Chem. Eng. J.,* 2009, vol. 147, p. 71.
7. Xiaowei, P., Ye, H.Y., Liangyu, Y., Pan, Y., Junling, W., Rong, X., Mary, B., and Chan-Park, *Carbon*, 2010, vol. 48, p. 2501.
8. Liang, L., Yu, H., Guoping, Y., Fangjun, L., Zhiliang, H., and Zhibin, M., *Mater. Lett*., 2009, vol. 63, p. 8.
9. Behzad, R., Shadpour, M., and Mahmood, T., *J. Power Sources*, 2009, vol. 187, p. 605.
10. Di Wei and Tin Wing Ng, *Electrochem. Commun*., 2009, vol. 11, p. 1996.
11. Hayashi, S. and Hamagushi, H., *Chem. Lett*., 2004, vol. 33, p. 1590.
12. Masanari, O. and Hamaguchi, N., *Appl. Phys. Lett*., 2006, vol. 89, p. 2506.
13. Winkleman, A., Gudiksen, K.L., Ryan, D., Whitesides, G.M., Greenfield, D., and Prentiss, M., *Appl. Phys. Lett*., 2004, vol. 85, p. 2411.
14. Zhao, D., Wu, M., Kou, Y., and Min, E., *Catal. Today*, 2002, vol. 74, p. 157.
15. Sun Xuewen and Zhao Suoqi, *Chin. J. Chem. Eng*., 2006, vol. 14, p. 289.
16. Zhuravlev, O.E., Verolainen, N.V., and Voronchikhina, L.I., *Russ. J. Appl. Chem*., 2011, vol. 84, no. 7, p. 1158. DOI: 10.1134/S1070427211070068.
17. Kharitonova, E.V., Zhuravlev, O.E., Chervinets, V.M., Voronchikhina L.I., and Demidova, M.A., *Pharm. Chem. J*., 2012, vol. 46, no. 5, p. 266.
18. Hubert, V., Masanori, K., Shingo, T., and Hajime, M., *J. Chem. Phys*., 2009, vol. 131, p. 244705.
19. Martinez-Magadan, J.M., Oviedo-Roa, R., Garcia, P., and Martinez-Palou, R., *Fuel Proc. Technol*., 2012, vol. 97, p. 24.
20. Granovskii, A.A., *PC GAMESS/Firefly, Version 7.1.G. http://classic.chem.msu.su/gran/gamess/index.html.*
21. Kireev, V.V., *Vysokomolekulyarnye soedineniya* (Macromolecular Compounds), Moscow: Vysshaya Shkola, 1992.